A STUDY OF THE PRIMARY DECOMPOSITION OF COAL BY INFRARED SPECTROPHOTOMETRY AND BY CHLOROFORM EXTRACTION

by

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ABSTRACT

For the differential I-R technique described in this paper, two specimens of coal were prepared for runs in the infrared double beam spectrometer. One specimen was prepared for the coal as received from the mine and this was placed in the reference beam. The other sample was prepared from coal which had been heated in a pressure tight container to the softening temperature. This was placed in the sample beam. The differential infrared spectrometer pattern thus obtained enables one to observe the changes in the infrared range.

In the second phase of these tests the coal was heated to temperatures in the plastic range and then extracted with chloroform. The extract yield was run differentially versus the untreated coal in the infrared spectrophotometer. These tests indicated different band intensities than the untreated coal and also revealed some absorbtion bands which did not occur in the original coal or in the residue extract from the absorbtion process.

The extract yield data was also used for a kinetic study of the coal's primary decomposition. Activation energies thus obtained for the solid to plastic step of the reaction appear to be of the general order of magnitude of 20 to 30 k.cal/mole.

Acknowledgements

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Thanks are also expressed to the U. S. Steel Corporation, Columbia Division who supplied the coal samples for the tests.

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I. INTRODUCTION

The primary decomposition of coal is closely related to the quality of coke the coal will ultimately produce.

Coke and Coke Quality

Fuels and Combustion Handbook[9] defines coke as a "...fused, cellular, porus structure that remains after free moisture and the major portion of the volatile matter have been distilled from bituminous coal and other carbonaceous material by the application of heat in the absence of air or in limited supply." Chemistry of Coal utilization[10] states that about 15% of the total annual coal production has been coked for a number of years.

The required quality of the finished coke for blast furnace use is very loosely defined. Fuels and Combustion Handbook[9] states "The real answer is to be had only from the blast furnace." Chemistry of Coal Utilization adds, "The correct evaluation of blast furnace coke is still an unsolved problem."

Two tests which determine the strength and therefore the acceptability of the coke are the Drop Shatter (A.S.T.M. D141-48) and Tumbler (A.S.T.M. D294-50) Tests.

In the Shatter Test, 50 pounds of coke all over 2 inches in size are placed in a box and dropped four times from a height of 6

feet on a steel plate. The resulting product is sieved on 2, 1½, and 1 inch screens. The Shatter Index is the amount remaining on a given size screen.

In the Tumbler Tests coke is placed in a drum and rotated at a specified speed for a fixed length of time. There is statistical correlation between coke quality and the Shatter and Drum Tests.

The size as well as the strength of the coke is an important factor in the blast furnace. A uniform size of coke seems to produce the greatest void value and the best ratio of coke consumption per ton of iron produced.

There are many other tests for coke quality which include determinations of reactivity, density, combustability, absorbtivity, electrical conductivity and compression strength.

Tests to Determine Coking Quality

Determination of the rank of the coal proves to be a rough measure of the coal's coking quality. In general, the low volatile, bituminous coal produces the best coke. Most papers in this search indicate that coal with a carbon content in the 80% to 90% range produce the best coke.

Chemistry of Coal Utilization[10] lists nine types of tests to determine the coking quality. Those most often referred to in the literature are the Free Swelling, (A.S.T.M. D720-46) Giesler Plastometer and Dilatometer Tests.

Two types of Free Swelling Tests are Agglutinating and Agglomerating. In the Agglutenating Test, one gram of coal with

varying amounts of inert material is carbonized at 950 degrees C. The recorded results are the maximum weight of inert material per gram of coal that will produce a coke button which will sustain a 500 g. weight without crushing. In the Agglomerating Test, one gram of coal is heated at 950 degrees C. The tendency to swell and the ability to support a 500 g. weight are observed.

The Dilatometer testing method uses a piston on the coal, free to move as the coal swells on heating. The vertical displacement of the piston is recorded.

In the Giesler Plastometer Test a constant torque is applied on wire-like fingers in the coal throughout a temperature programmed heating process. Dial divisions of rotation of the torqued fingers in the coal are recorded versus temperature.

Data and Theories on the Coking Mechanism

The key to coking seems to be in the fluid behavior of the coal as it is heated. This pointed up by the Free Swelling and Plastometer Tests and, more recently, by the work of Dryden and Panchurst.[1] They discovered that a chloroform soluble product is formed near the softening temperature. They proved that this extracted portion was an important part of the plastic stage by three tests. In the first test a coking coal would not swell on heating after the extracted portion had been removed. Attempts to extract material from a non-coking coal did not result in a good yield of soluble product and the yield did not rise as the softening

temperatures were reached as it did in the coking coal. In the third tests, adding the extract yield to a non-coking coal produced softening and swelling properties in it which it did not possess prior to the addition. Further tests on the extracted portion indicated that the extract was more fluid on heating than the original coal. They found that the extract contained more hydrogen and less oxygen than the original coal. They also stated that an infrared spectra showed that both the extract and the residue resembled the original coal. The yield of extract was found to drop off rather sharply if softening temperatures were held for longer periods of time during the heating process.

There is a good deal of infrared spectrophotometric data on coal. Some of the points brought out by previous studies follow .

1. Four papers[5,6,7,11] all report heavy OH bands (2.7 to 3.1 microns) in high volatile matter, poor coking coal. This bond disappears on heating. In general, this bond does not appear in the spectra of higher ranked coals which have good coking characteristics. Several papers[2,7,11,12] all suggest that the low rank, high volatile matter coal's inability to coke is because of the strong linkages of these OH groups. J. K. Brown[6] however, states "The simple explanation that strong intermolecular forces associated with hydrogen-bonding restricted the ability of the weakly coking coal to become plastic and swell is not satisfactory and is not in accord with a number of facts known about the coking process (eg. the destruction of coking power by solvent extraction)."

2. H. H. Storch[11] indicates weathered and oxidized coals show a strong carbonyl (5.87 microns) band absorption. Kinkby, Lakey, and Sareant[16] find this a strong absorption band in low rank coals.

3. There is some confusion on the 6.19 micron band. H. H. Storch points out that it is hard to separate from the hydrogen bonded OH at 6.1 microns and 6.20 microns. He concludes, however that the absorption at 6.19 microns is a result of phenoxyl or quinoidal compounds. J. K. Brown[6] found the 6.19 micron absorption in all coals except anthracite. ?He identified the band with an aromatic ring frequency or with a carbonyl group. He does not believe this absorption indicates a phenolic group because the intensity of the absorption does not decrease with the carbon content in the coal.

4. Three papers[6,7,11] report a rather strong absorption in the 8 micron region. Two of these authors[6,11] state this is the result of aromatic oxygenated compounds. One of the papers suggests that this absorption indicates the presence of polycyclic quinone compounds. They find this absorption band quite stable for coal ranks 78% to 89% carbon.

5. Fridel and Queiser[5] report that kaolinite or an aromatic ether represent the 9.67 micron absorption band.

6. Several papers report that high background absorption increases with the rank of the coal and this background may be

caused by pi electrons[5] in condensed aromatic rings or by scattering.[7]

J. K. Brown[6] used infrared spectrophotometry to study a weakly caking coal and a coking coal heated to various temperatures. As a result of this study he suggested that the removal of the aliphatic hydrocarbons leaves unsatisfied edge valences which are satisfied by C-C cross links. This reaction, he believes, continues above 550 degrees C. (above which the high background opaqued his spectra) with a further loss of hydrogen from the ring systems.

Brown and Hirsch[7] found by use of X-Ray diffraction techniques that the number of condensed aromatic rings goes up rapidly for coals with about 87% carbon content. They report that 75% of the carbon in a coal containing a total of 85% carbon is in condensed aromatic rings.

A. Whitacker[12] using the data produced by the X-Ray technique, studied the fringe groups which satisfy the edge valences of the carbon rings. From the amount of unorganized material and from his computed number of edge valences he concluded that there is barely enough unorganized material to go around to satisfy the edge valences unless there are considerable direct linkages. His work indicates that fringe structures, for the most part, must be composed of rather simple groups.

Fitzgerald[13] made a kinetic study of the plastic zone reaction, evaluating the reaction velocity from the Giesler Plastometer data. He points up the fact that fluidity is a function of

both temperature and time because at a constant temperature the fluidity goes to a maximum and then falls off. He observed that this indicates a decomposition reaction, first to a fluid, and then a decomposition of the fluid to solid and volatile products. He used the Arrhenius rate equation and found the activation energy for several coals to be 50 k. cal/mole. He found a reasonably good correlation between reaction velocity and the $1\frac{1}{2}$ inch Shatter Index, and suggested that the use of maximum fluidity with the reaction velocity should produce better results.

Two authors[7,11] comment that the strength of the coal (Young's Modulus, grindability, hardness, and viscosity) are at a minimum in the good coking coals.

II. INFRARED SPECTROPHOTOMETRIC STUDY OF COAL HEATED TO THE PLASTIC STAGE

Procedure in the Preparation of Samples

Coal specimens were prepared for evaluation by means of infrared spectrophotometry. The samples were ground to a very fine powder and then thoroughly mixed in carefully weighed proportions with potassium iodide (usually 6mg. of coal per gram of KI). A measured quantity of this mixture was then pressed in an evacuated die into plates for examination. The reliability of this technique has been well established in other systems.[2,3,4] Infrared specta were obtained using a Perkin Elmer Model 21 double beam recording spectrophotometer.

In the first tests the infrared absorbtion spectrum was obtained for three coals with a high fluidity (Giesler Plastometer dial divisions greater than 100) and for three coals with poor fluid properties (Geisler Plastometer dial divisions less than three). Most of the spectral assignments have been made in previous studies. Table II lists the spectral assignments used in this study.

Discussion of Results

For the 2.7 to 3.10 micron band the non-fluid coals showed stronger absorbtion indicating more OH groups in these coals. This

was in agreement with the findings of previous investigators.[5,6,7,11] Two of the fluid coals showed some carbonyl bonds (5.87 microns). None of the other coals absorbed in this region. All of the coals absorbed strongly at the 6.19 micron band again in agreement with the previous investigations. In the 8.0 micron region all coals showed weak absorbtion. None of the coals tested absorbed at the 9.05 micron ether band. The fluid coals indicated some absorbtion in the 9.67 micron ether region. This study was limited to the shorter wave lengths, and the more specifically assigned bands.

The results of this series of tests indicated that the spectra of the coals of the Rocky Mountain Region are similar to the spectra of the coals of the other parts of the world. The spectra also point up the fact that while some indication of a coal's fluid properties may be obtained from the infrared pattern, these data are not sufficient to evaluate the fluid properties of the coal.

Procedure for Differential I-R Examination of Heated Coal

The coal used for the second tests in this series was a blending coal used in coke ovens. The physical properties of this coal are shown in Table I. One sample was prepared from the coal as received from the mine. The other sample of coal was heated in a pressure tight container to the fluid range: this required approximately 20 minutes. The temperature in the fluid range was held for periods

Table 1. Physical Properties of Coal Used in Differential Infrared Spectrophotometer Tests

Proximate Analysis		Ultimate Analysis		Gieseler Type Plastometer	
H_2O	2.94	C	75.20	Initial Soften. Temp.	341°C
V. M.	30.53	H_2	5.23	Max. Fluidity Temp.	422°C
F. C.	58.17	N_2	1.63	Max. Dial Div./Min.	2,977
Ash	11.30	Ash	11.30	Solidification Temp.	469°C
Sulfur	0.82	S	0.82		
		O_2	5.82		

Table II. Spectral Assignments for Coal

Microns	
2.74 - 2.78	Free OH stretching
2.82 - 3.10	OH stretching, intermolecular hydrogen bonds
3.30	Aromatic CH, weak
3.42 - 3.49	Naphthenic and/or aliphatic CH bonds
5.87	C===O band, weak shoulder
6.19	Very intense band; may be partly caused by a conjugated carbonyl structure such as in quinones
6.90	CH_2 groups
7.25	CH_3 groups
9.05	Ether band
9.67	Aromatic band, intense in aromatic ethers

of time from 10 to 30 minutes with all time lengths producing the same general spectra. The sample was then quenched and prepared as previously described.

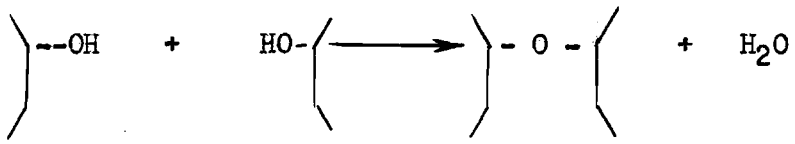
The plate containing the untreated coal was placed in the reference beam of the spectrophotometer and the plate containing the coal which had been heated was placed in the sample beam. A differential absorption spectra was thus obtained.

To prove the reliability of the differential spectrophotometer method, two samples of untreated coal were prepared and one was placed in the reference beam and the other placed in the sample beams. The pattern obtained is shown in Figure 2. The virtual absence of absorption maxima substantiated the reliability of the differential technique and the data obtained from it.

Discussion of the Results of the Heated Coal Series

Figure 1 shows a typical spectrum obtained by the differential technique. Since the coal sample which had been heated was placed in the sample beam, peaks downward on the pattern indicated vibrational spectra for bonds greater in number in the heated coal and peaks upward indicated the presence of a greater number of bonds in the untreated coal sample. Increases were noted in the 2.7 to 3.10 (OH stretching) micron range, 3.3 to 3.4 micron (aromatic hydrocarbon), 7.25 micron (hydrocarbon bending, CH_3) and 9.67 micron (aromatic ethers).

The increases in aromatic ether bonds suggest the following mechanism.



Other studies show that coal is primarily composed of condensed aromatic rings. Experimental work discussed later in this paper and by others[8] indicates that the final coke satisfies these edge valences with C - C linkages. This suggested mechanism is based on the theory that heating coal is a continuous change of edge groups and edge bonds of these rings. Some hydrogen would of course be available from the decomposition of the CH groups. An aromatic ether could be a fluid in the softening temperature range. The action of this fluid could provide greater mobility for the rings which, in turn, may result in a better, final orientation of the crystallites. This action would make a greater number of C - C bonds and consequently a stronger coke.

The increases in the aromatic (3.3 micron - 3.4 micron) bond substantiates the general theories of the coking mechanism which suggest changes to the aromatic and ultimately to a graphitic structure. There does not seem to be any ready explanation for the increase in the CH_3 band. This, too, may represent a change in edge groups. The CH_2 band shows a decrease. The 5.87 micron (C=O) and the 6.19 micron (C=O-quininoid) bands are shown to increase; however, some of the tests indicated a decrease. It would seem most probably that the C=O band does decrease, however the possibilities of H_2O also contributing to one of these bands (6.19 micron) and of possible oxidation of the

sample after removal from the container seems the best explanation for the behavior of these bands. No attempt was made to interpret bands of wave lengths greater than 9.67 micron except to note their general increase, again substantiating the polymerization-graphitization theory.

I-R Spectra Examination of Coal Heated in a Closed Crucible

Other tests were run in a closed crucible, heated rather quickly to temperatures in the fluid range. Samples were prepared as before and were run against a blank of KI in the reference beam. Figure 3 shows the results of these tests. Here the general decrease in the bands assigned to typical edge groups is noted. One should call attention, however, to the tendency for the OH and aromatic ether groups to increase before finally decreasing at the higher temperatures.

The two techniques differ, of course, in that in the second method the decomposition materials are allowed to escape. It is felt that the first (pressure-tight container) method is a more powerful tool for the study of the softening stage because it provides a means for examining the bonds as they occurred in that stage before subsequent decomposition.

X-Ray and I-R Examination of the Char

Although the char resulting from Free Swelling tests when prepared for examination by infrared spectrophotometry produced a high

background in the infrared absorbtion region, one sample was prepared and successfully run using 3 mg. of coal per sample. The response was good throught the range of frequencies. The absorbtion pattern obtained from this test showed no absorbtion peaks, indicating a final graphitic structure with C-C bonds.

The belief that coke is of a graphitic structure was substantiated by powdering the char obtained from the coke buttons and examining the sample by means of X-Ray diffraction. The coke button powders showed the same general X-Ray reinforcement peaks as graphite. These X-Ray diffraction patterns were also used to calculate the crystallite size. These calculations showed the crystallite size for the fluid coal to be approximately 1.5 times greater than that for the non-fluid coal.

III. INFRARED SPECTROPHOTOMETRIC STUDY OF THE CHLOROFORM EXTRACTION OF HEATED COALS

Procedure

The coal used for these tests was again a blending coal used in coke ovens. Some physical properties of this coal are shown in Table I. The coal was heated in a pressure tight container to a temperature of 370°C in approximately 25 minutes with a period of 10 minutes at the final temperature. The sample was quenched and then extracted in a soxhlet apparatus with chloroform. The chloroform was then allowed to evaporate at room temperature leaving the extract yield. This procedure was similar to that of Dryden and Panchurst except that in these tests a pressure tight container was used as opposed to the unsealed quartz container used by Dryden and Panchurst. It was felt that by using the closed, higher pressure system, a more plastic state would result and that this state would remain for a longer period of time during heating.

Coal specimens were prepared for evaluation by means of infrared spectrophotometry by the technique described in previous tests. Infrared spectra were obtained using a Perkin Elmer Model 21 double beam recording spectrophotometer. Differential spectra were obtained by placing one sample in the reference beam and another specimen in the sample beam. As in the previous differential tests, peaks

downward on the pattern indicated vibrational spectra for bonds greater in number in the specimen in the sample beam, and peaks upward indicated the presence of a greater number of bonds in the sample in the reference beam. Figures 4,5,6, and 7 show some of the spectra obtained from these tests.

Discussion of the Spectra

Table II lists the spectral assignments used in this study. The spectra obtained for the extract residue Figure 4 is similar to the spectra of the untreated coal, Figure 1.

1. The differential spectra of Figure 3 shows in the OH stretching region the extract contains less free OH and more intermolecular hydrogen-bonded OH than the untreated coal.

2. Absorption in the 3.3 micron and 3.42-3.49 micron hydrocarbon bands shows greater quantities of this material in the extract.

3. In the 5.87 micron and 6.19 micron carbonyl region, the 5.87 band shows an increase in the extract. The 6.19 band shows a rather indefinite change with the suggestion of some new bands in that region. The apparent bands at 6.03 and 6.20 microns probably result from absorption by OH bonds.

4. The 6.90 micron and the 7.25 micron bands (CH_2 and CH_3) show greater strength in the extract as would be expected from the 3.3 micron and 3.42-3.29 micron bands and from previous work[1] which show that the extract contains more hydrogen than the untreated coal.

5. The 9.05 micron and 9.67 micron ether bands indicate the extract contains more of the 9.05 vibrational absorption bands and less of the 9.67 micron bands.

6. The extract also absorbs at four frequencies for which there is no absorption in the untreated coal or in the residue. These bands are at 6.6, 7.43, 8.47, and 10.55 microns.

The 6.6 micron region most probably represents an aromatic structure created by the softening reaction. The 7.43 micron band may represent an OH group for which there have been indications in the 3 micron and 6.19 micron region. In terms of what has been previously observed, perhaps CH_2OH would be the most probable identification for this band. A PhCHO compound could account for the absorption in the 8.47 and 19.55 micron wave lengths.

Taking a broad look at the extraction patterns there are many indications of reactions of increases in the molecular OH groups, and in the ether groups. This could be explained by a reaction in which OH groups satisfy an edge group valence early in the reaction finally yielding to the single bonded oxygen of the ether group with H_2O leaving the system.

It may also be noted that most of the bands are increased in intensity in the extract. It seems reasonable to assume these bands are for the most part edge groups on carbon ring structures. This would indicate the extract and, in turn, the fluid portion contain more of these edge groups. This suggests that the extract, probably

the more significant portion of the plastic component, contains the lower molecular weight compounds. This group of molecules would have more edge valences to be satisfied, thus explaining the additional bonds indicated in the extract.

IV. KINETIC STUDY OF THE FORMATION OF A CHLOROFORM SOLUBLE MATERIAL

Theory

The following reaction mechanism is proposed for the primary decomposition of a coal with fluid properties.

$$A \longrightarrow P \quad (1)$$
$$P \longrightarrow SC + G_1 \quad (2)$$

This mechanism is similar to the mechanism proposed by Chermin and van Krevelen[15]. A, represents the untreated coal; P. the plastic stage; SC, the semi-coke and G_1, the low temperature gas products from the primary decomposition.

In these tests chloroform extraction was used to determine a value proportional to the amount of P produced. The relationship between the plastic stage and the extract yield seems to be well established by Dryden and Panchurst[1] who showed that the residue does not produce a fluid stage when the extract has been removed.

Procedure

The coal was heated in a pressure tight container as in previous tests. In order to get reproducibility it was found that

the heating rate must be carefully controlled. Optimum characteristics required of the heating process were a rapid rise in temperature to the maximum temperature for the test and for maintenance of this temperature for a time to produce the greatest extract yield. The rapid temperature rise was important to minimize reactions before the maximum temperature was reached and because a rapid temperature rise usually accentuates the plastic stage and the coking properties of the coal. It was desirable to hold the maximum temperature for a time which would produce a maximum yield in order to relate one run to another and to minimize the effect of errors. After some preliminary tests the heating pattern that seemed most nearly to satisfy the preceding conditions was a total heating time of 32 minutes, with the temperature in the range of the last ten percent of the temperature rise for approximately forty percent of the heating time. This system was used for all the heating processes reported in this study.

After heating, the sample was extracted with chloroform and evaporated as in the previous extraction tests. The yield of extract was determined and a plot of yield versus temperature was made (Figure 8). In this plot the temperature used was the mean temperature for the final ten percent of the temperature rise.

Discussion of Results

Figure 6 shows a plot to determine the order of magnitude of the activation energy of step 1 of the proposed model. This study utilized the following relationships:

$$\frac{\%\ \text{yield}}{\text{Heating Time (constant)}} = kB$$

$$k = B_1 e^{-E/RT}$$

Therefore

$$\ln.kB = \ln(\text{constant}) - E/RT$$

where k is the reaction rate constant, B and B_1 are constants, E is the activation energy for the step involved, R the gas constant and T the absolute temperature in degrees K.

It follows that on a plot of the rate constant versus 1/T such as Figure 9, the slope of the curve must represent E/R. In this plot the low temperature range has the greatest significance since it may be assumed that in this temperature range step 2 is negligible. This plot indicates an activation energy for the initial step of 12 k cal/mole and 20 k cal/mole for the second step assuming the second step is controlling beyond the point of maximum yield.

It has been established by van Krevelen, van Heerden and Huntjens[14] that the activation energy for the primary gasification (E_2) is equal to approximately 50 k cal/mole for all coals. Chermin and van Krevelen[15] propose that unless E_1 is approximately equal to E_2 the coal will not have a plastic stage which will contribute to a satisfactory coke product. The value of E_1 and E_2 determined by these tests does not appear to agree with previously established values. A plot similar to Figure 9 using the data of Dryden and Panchurst[1] reveals activation energies of the same order of magnitude as for this study.

Some observations of the physical properties of the coal as it was removed from the heating process deserve some mention here. The heated coal appeared much the same as before heating (rather finely ground) up to the point of maximum yield. At or near the point of maximum yield the coal sample was caked but not swelled. Higher temperatures produced a swelled sample with a relatively high swelling index.

V. CONCLUSIONS

The use of the infrared spectrophotometry and the extraction techniques have indicated the following information regarding the primary decomposition of the coal.

1. The heated coal and the chloroform extract show appreciable increases in the molecular OH bonds.

2. The chloroform extract yield shows a higher hydrocarbon content than the untreated coal. This is particularly significant since extraction was after heating to temperatures at which some hydrocarbons leave the material as a gas. The extract must consist of the lower molecular weight portions of the plastic material of the coal. This reasoning would imply that the extract is composed of smaller numbered carbon ring compounds with a large number of hydrocarbon edge groups.

3. Both the extract and the heated coal show marked changes in the carbonyl and ether absorbtion region. The results of this study alone are not sufficient to discuss these changes except in a general way. It appears that there is a shift from the carbonyl bonds toward ether bonds as the coal is heated. A mechanism may be proposed which includes this change and the increase in the molecular OH bonds.

4. The extract shows absorbtion at four or more bands for which there is no absorbtion in the untreated coal. These absorbtions

appear to substantiate the belief that there are increased molecular OH bonds in the heated coal.

5. There is an eventual disappearance of all or almost all of the bonds except the C-C bonds as the coal is heated to the coking temperatures. The final product has a graphitic structure with the more fluid coals showing a larger crystallite size.

6. A kinetic study of the initial reaction which results in a plastic state for the coal indicates activation energies for of approximately 12 k cal/mole for the first step of the decomposition process and 20 k cal/mole for the second step of the proposed mechanism.

It is the author's opinion that the conclusions which may be drawn from the results of these tests are less important than the direction of study of which they seem to point. As newer techniques such as these are developed and as more data become available from these techniques, a more specific understanding of the primary decomposition of coal will be possible. A good understanding of the activation energies of the primary decomposition of the coals involved could change the blending of coals to produce good coke from its present empirical stage to a much more exact science.

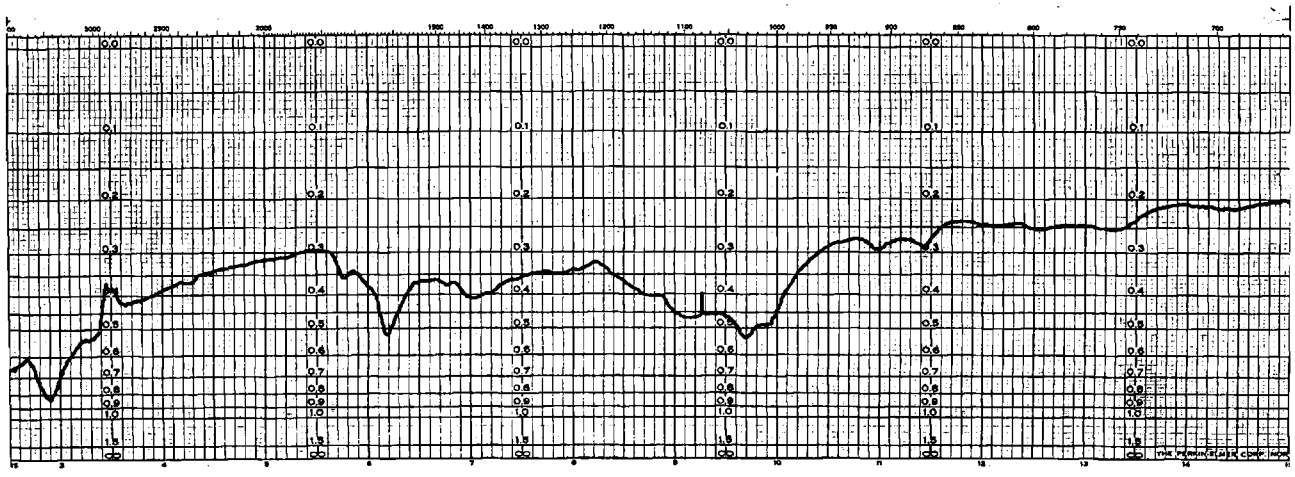
VI. RECOMMENDATIONS

The studies presented in this report represent only a beginning in the use of the techniques described to study the primary decomposition of coal. Infrared absorbtion bands must be more positively identified, particularly those for the extract yields, for a fuller understanding of the data obtained by this technique and more data is necessary for a more thorough kinetic study.

For a better identification of the spectral bands in the extract, a fractional distillation might be helpful. Gas chromotography and mass spectrometry could be used to identify the lighter fractions of the extract.

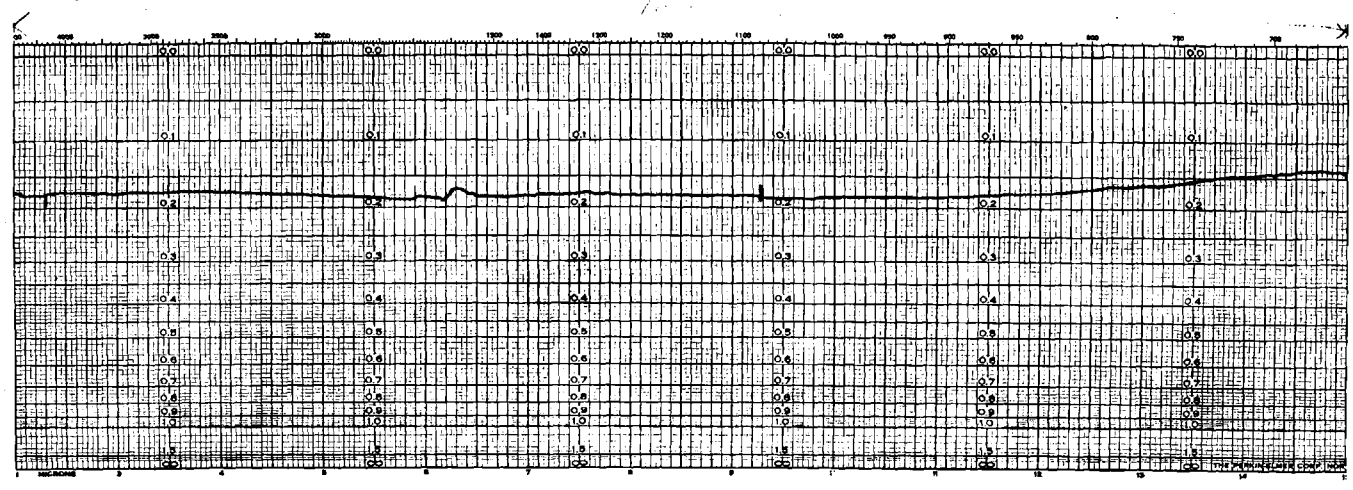
The data which are necessary for a good kinetic study must include the extract yield as a function of temperature which was determined in this study and also the extract yield as a function of time as a constant temperature. Since the plastic stage represented by the extract yield is decomposing as well as forming, the amount of the decomposition or weight change of the sample must be obtained also. The author plans to obtain these required data by the use of vertical furnace in which weight changes may be recorded as a function of time. A much more thorough kinetic study should be possible when the additional data are available.

APPENDICES



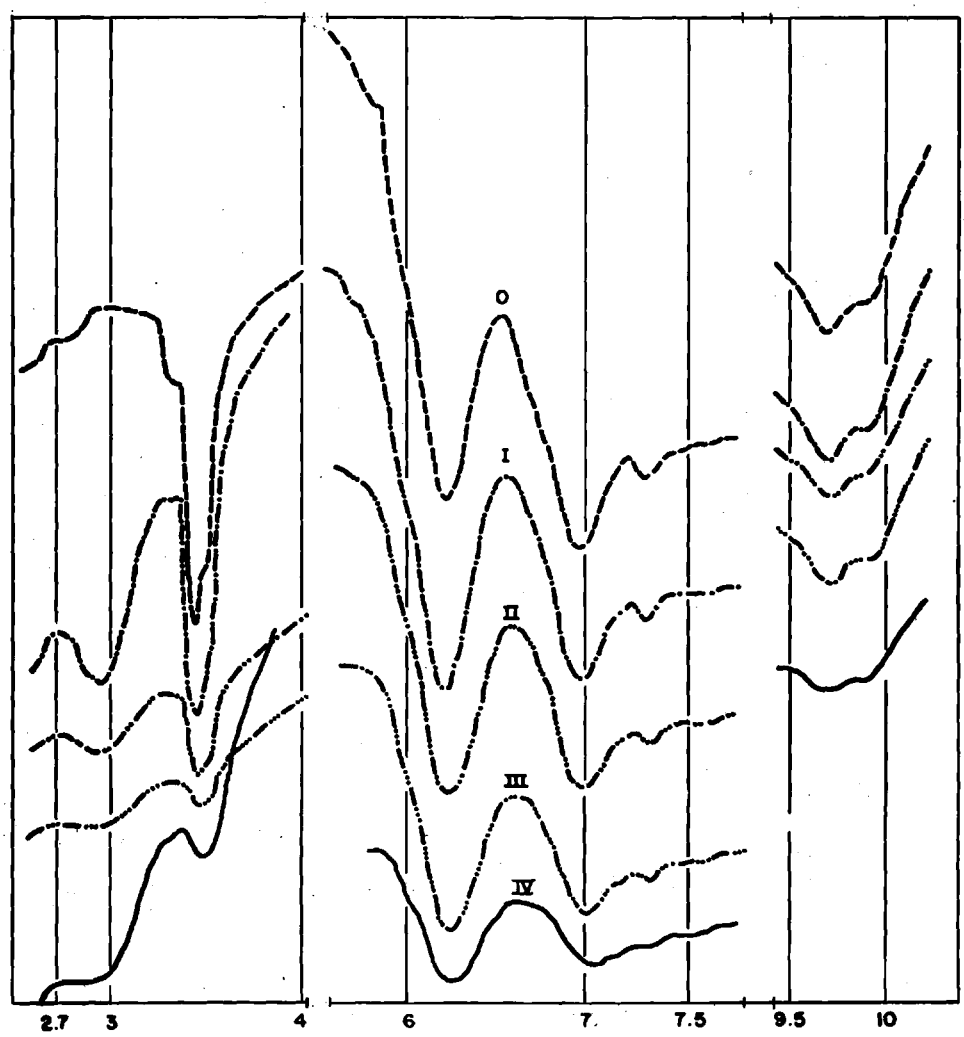
WAVELENGTH IN MICRONS

Figure 1. Differential infrared spectrophotometric pattern. Untreated coal in the reference beam; coal heated to the softening range in the sample beam.



WAVELENGTH IN MICRONS

Figure 2. Differential infrared spectrophotometric pattern to prove technique. Untreated coal from the same sample in both the reference and sample beams.



——0 - Furnace at 500°F, coal sample 1 gram —·—II - In furnace 2 minutes
—·—I - In furnace 1 minutes ——III - In furnace 3 minutes
——IV - In furnace 5 minutes (max. coal temperature approximately 475°C.

Figure 3. Infrared spectrophotometric pattern of coals heated in a closed crucible.

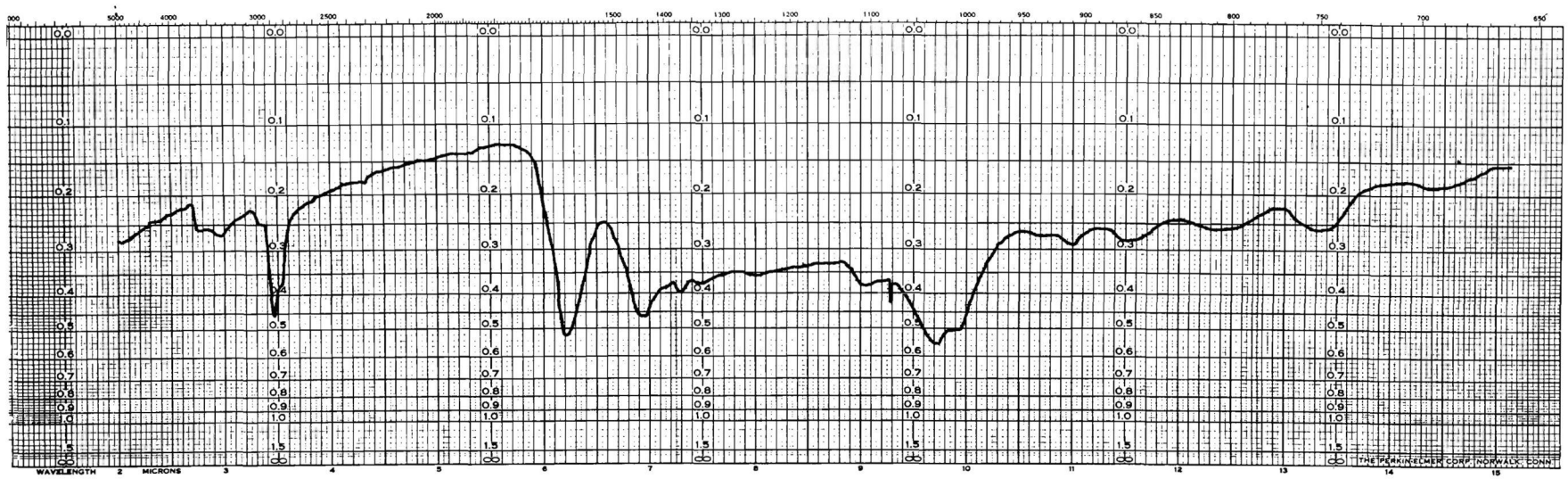


Figure 4. Untreated coal vs. potassium iodide blank.

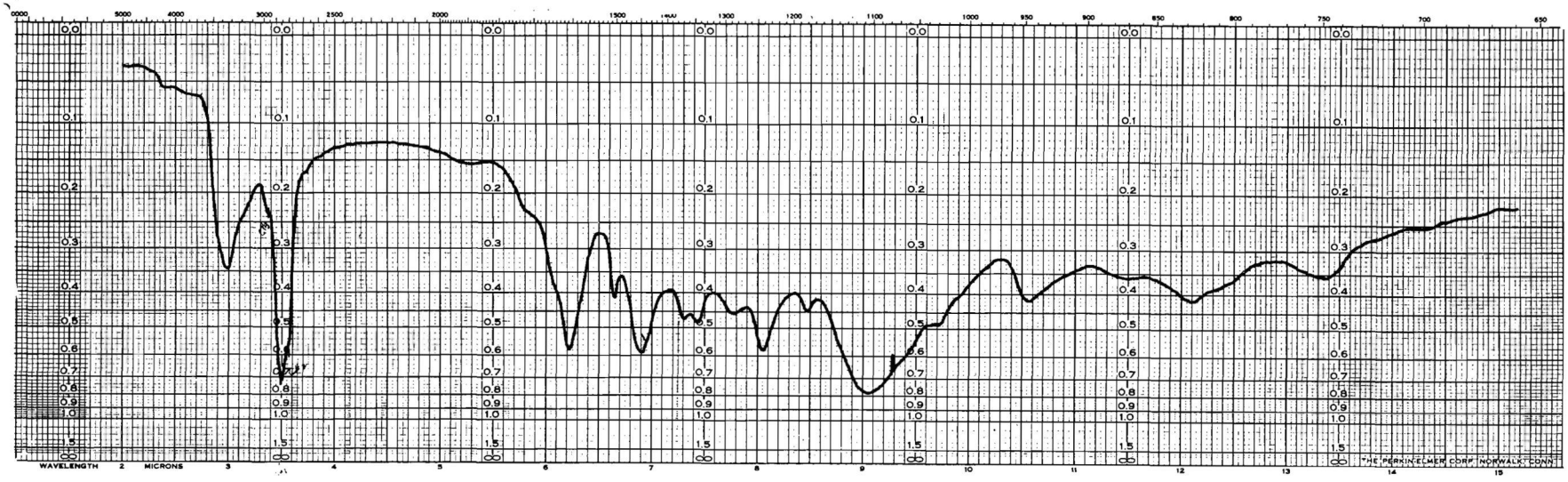


Figure 5. Chloroform extract yield vs. blank.

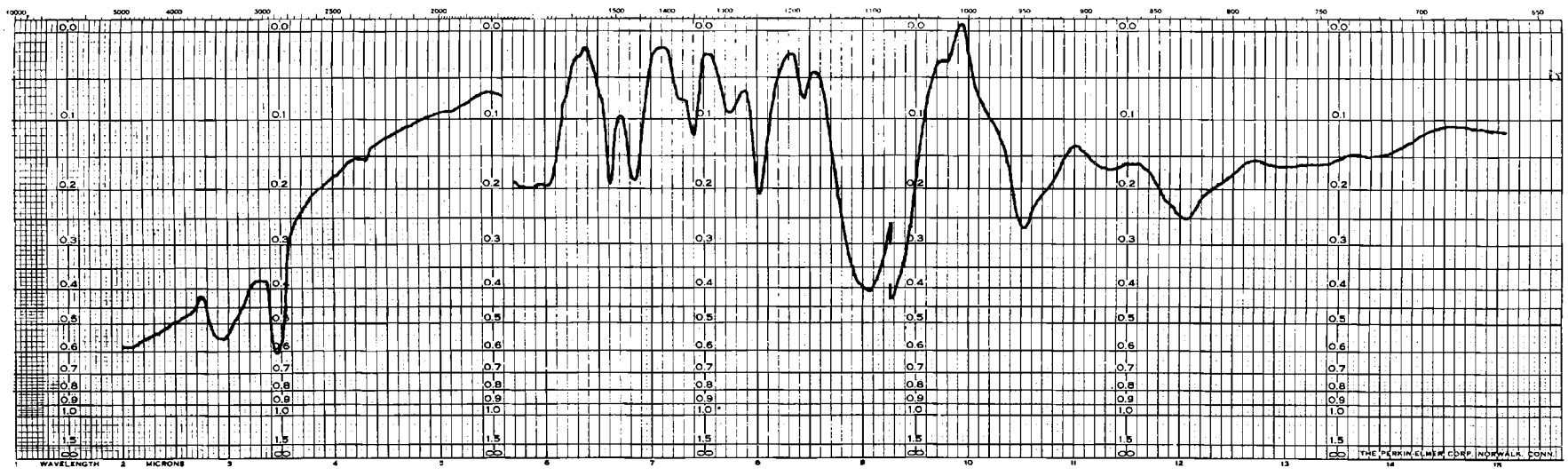


Figure 6. Untreated coal reference beam. Chloroform extract yield sample beam.

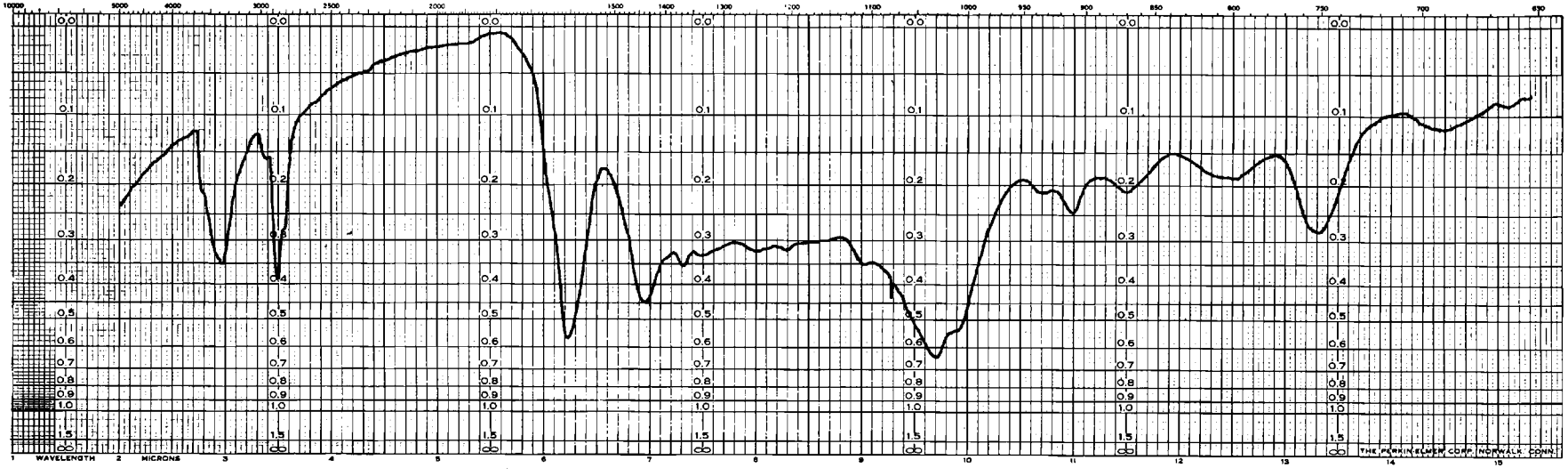


Figure 7. Extract residue vs. potassium iodide blank.

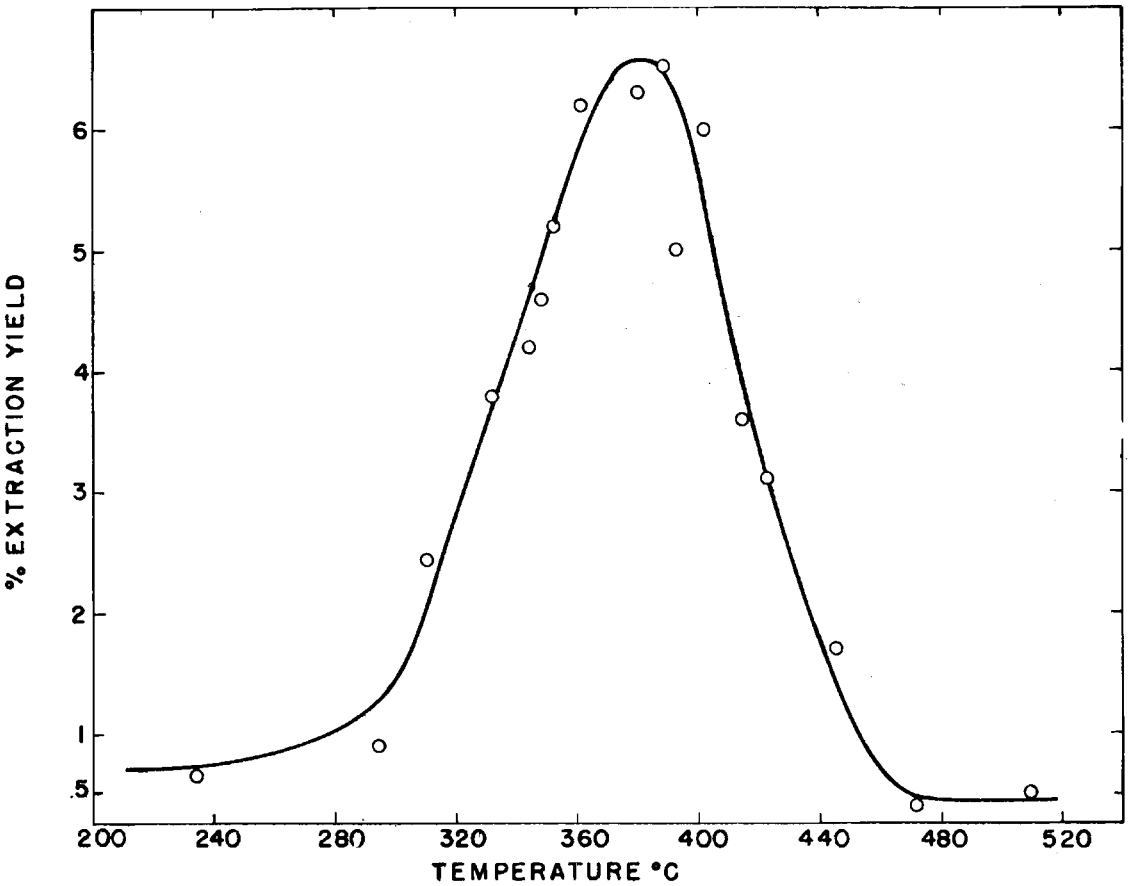


Figure 8. Chloroform extraction yield vs. temperature.

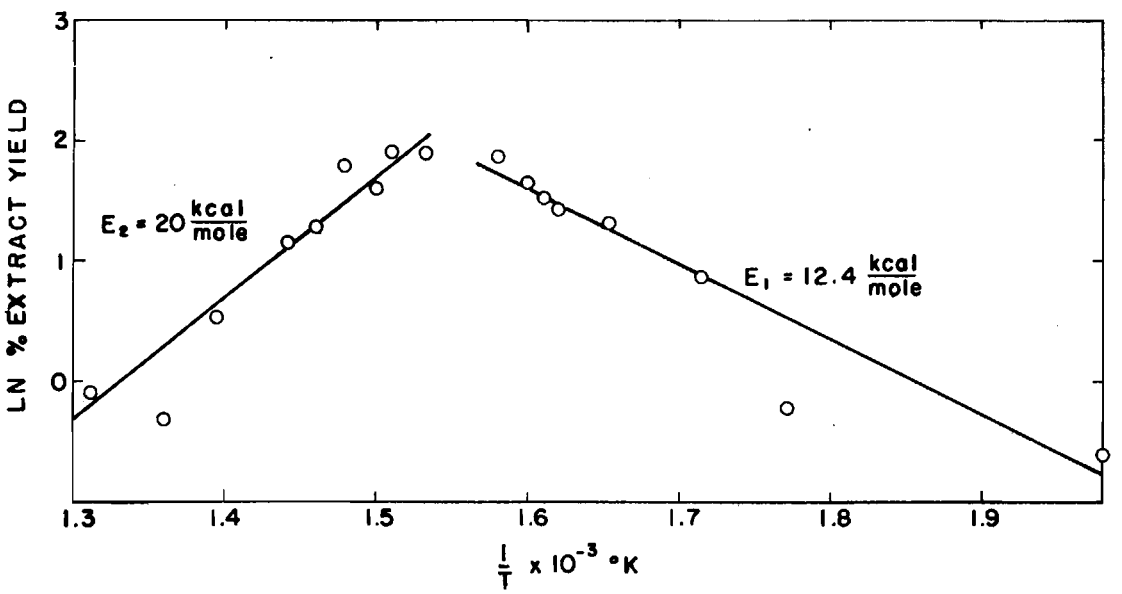


Figure 9. Ln. % extraction yield vs. 1/T to determine activation energies.

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A STUDY OF THE PRIMARY DECOMPOSITION OF COAL BY INFRARED SPECTROPHOTOMETRY AND BY CHLOROFORM EXTRACTION

by

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An abstract of a thesis submitted to the faculty of the University of Utah in partial fulfillment of the requirements for the degree of

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ABSTRACT

For the differential I-R technique described in this paper, two specimens of coal were prepared for runs in the infrared double beam spectrometer. One specimen was prepared for the coal as received from the mine and this was placed in the reference beam. The other sample was prepared from coal which had been heated in a pressure tight container to the softening temperature. This was placed in the sample beam. The differential infrared spectrometer pattern thus obtained enables one to observe the changes in the infrared range.

In the second phase of these tests the coal was heated to temperatures in the plastic range and then extracted with chloroform. The extract yield was run differentially versus the untreated coal in the infrared spectrophotometer. These tests indicated different band intensities than the untreated coal and also revealed some absorbtion bands which did not occur in the original coal or in the residue extract from the absorbtion process.

The extract yield data was also used for a kinetic study of the coal's primary decomposition. Activation energies thus obtained for the solid to plastic step of the reaction appear to be of the general order of magnitude of 20 to 30 k.cal/mole.